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## Kinetics Studies of Radical-Radical Reactions (I): The $\text{NO}_2 + \text{N}_2\text{H}_3$ System

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The state-of-the-art hypergol combination currently used in the US for many space propulsion applications consists of monomethyl hydrazine, as the fuel, and nitrogen tetroxide, as the oxidizer. The Air Force Research Laboratory is developing new hypergolic fuels which will provide enhanced performance capabilities as well as improved affordability and efficiency. Furthermore, handling of these new hypergolic fuels is also expected to have a much smaller logistical footprint due to the fact that they are being designed to be environmentally benign. However, practical realization of these hypergols in spacecraft propulsion systems will only come after attaining a satisfactory understanding of how to optimize their combustion characteristics in relevant operating environments. Here we report theoretical results obtained on the prototypical radical-radical reaction:  $\text{NO}_2 + \text{N}_2\text{H}_3$ , and the progress made towards building an apparatus consisting of laser photolysis/fast flow-tube reactor coupled to a mass spectrometer for investigating the kinetics of this elementary reaction.

*Keywords:* Hypergolic, Propellants,  $\text{N}_2\text{H}_3$ , Kinetics, Mechanism.

### 1. Introduction

The hydrazine ( $\text{N}_2\text{H}_4$ ) and dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) reaction system is widely used as liquid propellants for satellite and space propulsion applications.<sup>1</sup> As an oxidizer, the  $\text{N}_2\text{O}_4$  molecule is known to have several inter-conversion structural conformers:  $\text{NO}_2$  monomer, symmetric  $\text{N}_2\text{O}_4$  dimer with  $\text{D}_{2h}$  symmetry, asymmetric  $\text{ONONO}_2$  with cis- and trans-structures, and the van der Waals complex with  $\text{C}_{2v}$  symmetry.<sup>2</sup> Recently, Lai et al.<sup>3</sup> theoretically studied the reaction of  $\text{N}_2\text{H}_4$  with the  $\text{N}_2\text{O}_4$  isomers and reported that the reaction of  $\text{N}_2\text{H}_4$  with sym- $\text{N}_2\text{O}_4$  ( $\text{D}_{2h}$ ), cis- $\text{ONONO}_2$  ( $\text{C}_s$ ), and  $\text{NO}_2$  has to overcome an activation barrier of 14.2, 10.6, and 7.6 kcal/mol, respectively. However,  $\text{N}_2\text{H}_4$  can spontaneously react with trans- $\text{ONONO}_2$  ( $\text{C}_s$ ) and cis- $\text{ONONO}_2$  ( $\text{C}_1$ ) to produce  $\text{HONO}_2 + \text{H}_2\text{NN}(\text{H})\text{NO}$  with a rate constant of  $4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 250 K. The intermediate  $\text{H}_2\text{NN}(\text{H})\text{NO}$  thus formed can rapidly fragment to produce the reactive radical  $\text{N}_2\text{H}_3$  with a rate constant of  $1 \times 10^7 \text{ s}^{-1}$  at 1000 K, which is fast enough to initiate the hypergolic chain

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reactions of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ . Consequently, the kinetics of  $\text{N}_2\text{H}_3$  with  $\text{NO}_2$  is important for understanding the mechanism and the ignition process of the hydrazine and  $\text{N}_2\text{O}_4$  system. However, the reaction is complicated by multiple radical-radical abstraction, addition and subsequent dissociation pathways. In this work, the reaction of  $\text{N}_2\text{H}_3$  with  $\text{NO}_2$  was studied by *ab initio* multi-reference second-order perturbation theory and quadratic configuration interactions and coupled-cluster theories. It was found that oxidation of the  $\text{N}_2\text{H}_3$  radical by  $\text{NO}_2$  occurs with submerged barriers with relatively large exothermicities. Consequently, the accuracy of the value of the theoretical rate coefficient computed for this reaction will greatly depend on the level of accuracy employed to describe the electron correlation effects for both the outer and multiple inner transition states.<sup>4</sup> We have accurately characterized the potential energy surface for the  $\text{NO}_2 + \text{N}_2\text{H}_3$  system and have established the most likely reaction mechanism. The technique of laser photolysis/fast flow-tube reactor coupled to a mass spectrometer is also being utilized to experimentally investigate the reaction kinetics of this system.

## 2. Theoretical and Computational Details

Due to electron repulsion between the electronegative oxygen and nitrogen atoms in this reaction system, the multi-reference character of the wavefunction is quite strong. Therefore, we have used multi-reference second-order perturbation theory (CASPT2) with Dunning's augmented correlation consistent basis set, aug-cc-pVDZ to optimize the geometries of the stationary points of the potential energy surface and to calculate the corresponding ro-vibrational frequencies. For the reactants ( $\text{N}_2\text{H}_3$  and  $\text{NO}_2$ ) and the products (NNH<sub>2</sub>, cis-NH=NH, and trans-NH=NH), the larger basis set, aug-cc-pVTZ was applied, and all of the electrons were included in the active space. The geometries of the products (cis-HONO, trans-HONO, and HNO<sub>2</sub>) were optimized at the CASPT2/aug-cc-pVDZ level, with all the electrons included in the active space. For the transition states, the active space was selected to describe adequately the bond breaking/making process of interest with reasonable computational efficiency. Specifically, for H-abstraction from  $\text{N}_2\text{H}_3$  by  $\text{NO}_2$  to form cis-HONO and the NNH<sub>2</sub> diradical, the transition state was optimized using an active space (6e,8o) consisting of  $\sigma$  bonding and anti-bonding pairs of the imidogen-H being abstracted,  $\pi$  bonding and anti-bonding pairs of the N–N bond,  $s$  orbital of the electron-deficient N atom on NNH<sub>2</sub>, and  $\sigma$  bonding of the O–H bond being formed. For H-abstraction from  $\text{N}_2\text{H}_3$  by  $\text{NO}_2$  to form cis-HONO and trans-NH=NH, the transition state was optimized using an active space (6e,6o) consisting of  $\sigma$  and  $\pi$  bonding and anti-bonding pairs of N–O bond,  $p$  orbital of the O atom that is interacting with the H being abstracted and its corresponding virtual orbital. Furthermore, the (6e,8o) active space was used for optimization of the addition adducts and H-bonded complexes.

Higher-level stationary point energies were obtained from quadratic configuration interactions and coupled-cluster theories with single and double excitations, and correction for triple excitations. Specifically, the QCISD(T) and CCSD(T) calculations employed the correlation-consistent, polarized-valence, triplet- $\xi$  (cc-pVTZ) and quadruple- $\xi$  (cc-pVQZ) basis sets of Dunning.<sup>5,6</sup> The energies were then extrapolated to the complete basis set (cc-pV $\infty$ Z) limit<sup>7</sup> by the asymptotic form.<sup>8,9</sup> Electronic structure calculations were performed using the MOLPRO<sup>10</sup> quantum chemistry package.

### 3. Experimental Details

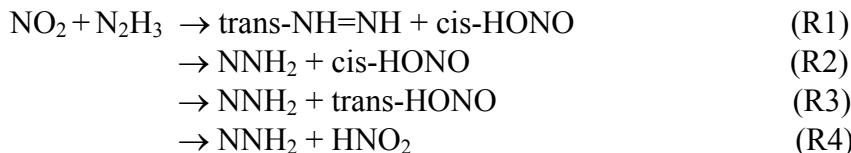
A halo-carbon wax coated Pyrex flow-tube reactor which was 100 cm long with internal diameter of 2.54 cm was used.  $\text{N}_2\text{H}_4$  vapor and gaseous  $\text{NO}_2$  were carried into the flow-tube using excess nitrogen gas. The  $\text{N}_2\text{H}_4$  was photolyzed under optically thin conditions by sending a 193-nm laser beam along the axis of the flow-tube which had been fitted with appropriate quartz optical ports at both ends to produce  $\text{N}_2\text{H}_3$  radicals under excess  $\text{NO}_2$  conditions. The pressure of the flow-tube was typically held at  $\sim 2$  Torr and the linear flow velocity of the gas mixture adjusted to attain plug-flow conditions that gave reaction lengths ranging from 40 to 70 msec. The reaction kinetics of the  $\text{N}_2\text{H}_3$  radicals was followed in real-time by sampling the gas mixture through a small pin hole at the mid-point down the flow-tube axis using a skimmer that was attached to a differentially pumped chamber containing an electron impact ionization quadrupole mass spectrometer.

### 4. Results and Discussion

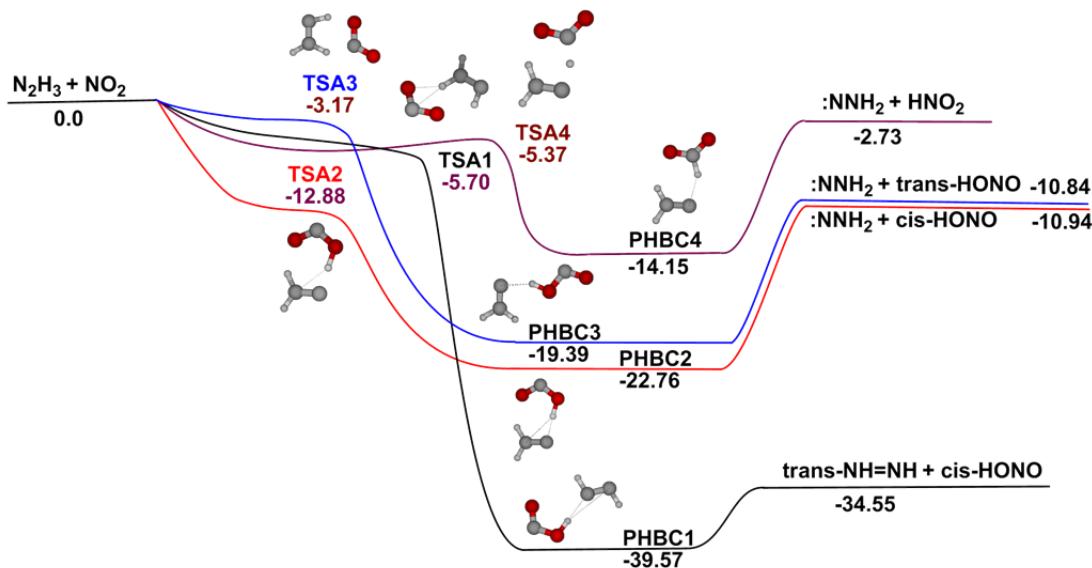
To our knowledge, experimental and/or theoretical studies on the kinetics of the reaction  $\text{NO}_2 + \text{N}_2\text{H}_3$  has not been reported in the literature. Recently, Liu et al.<sup>11</sup> studied the gas-phase chemistry of the hypergolic system, monomethyl hydrazine (MMH) with  $\text{NO}_2/\text{N}_2\text{O}_4$  at room temperature, and proposed that the oxidation of MMH by  $\text{NO}_2/\text{N}_2\text{O}_4$  at atmospheric pressure occurs via two mechanisms: (1) sequential H-abstraction and HONO formation, and (2) reaction of MMH with asymmetric  $\text{ONONO}_2$ , leading to the formation of methyl nitrate. Furthermore, they reported that all of the intermediates observed experimentally could be successfully explained by the above mechanisms. Furthermore, Catoire et al.<sup>12</sup> suggested that the addition products  $\text{CH}_3\text{N}(\text{NO}_2)\text{NH}_2$  and  $\text{CH}_3\text{N}(\text{ONO})\text{NH}_2$  are the major stable pre-ignition products which account for the formation of the white-yellow condensate.<sup>13</sup> However, in the study of Liu et al.,<sup>11</sup> these species were not identified as the major early species and the only major product observed is methylhydrazene,  $\text{CH}_3\text{N}=\text{NH}$ . This indicates that the direct H-abstraction reaction from the methylhydrazyl radical by  $\text{NO}_2$  leading to the formation of  $\text{CH}_3\text{N}=\text{NH}$  might be a more dominant path compared to the radical-radical addition path followed by subsequent decomposition of addition products. Consequently, this would suggest that this might also be the case for the analog reaction between  $\text{NO}_2$  and  $\text{N}_2\text{H}_3$ . In this work, the reaction pathways for both abstraction and addition in  $\text{NO}_2 + \text{N}_2\text{H}_3$  were theoretically explored at the CCSD(T)/cc-pV $\infty$ Z//CASP2/aug-cc-pVDZ level.

#### (I). Direct H-abstraction Reactions

The ground state of  $\text{NO}_2$  ( $^2\text{A}_1$ ) has  $\text{C}_{2v}$  symmetry. For direct abstraction of hydrogen from  $\text{N}_2\text{H}_3$ , hydrogen bonding plays an important role in the transition state geometries. It was determined that direct abstraction occurs via four different transition states, all with negative barriers (see Figure 1), to form the following products:



Unit: kcal/mol



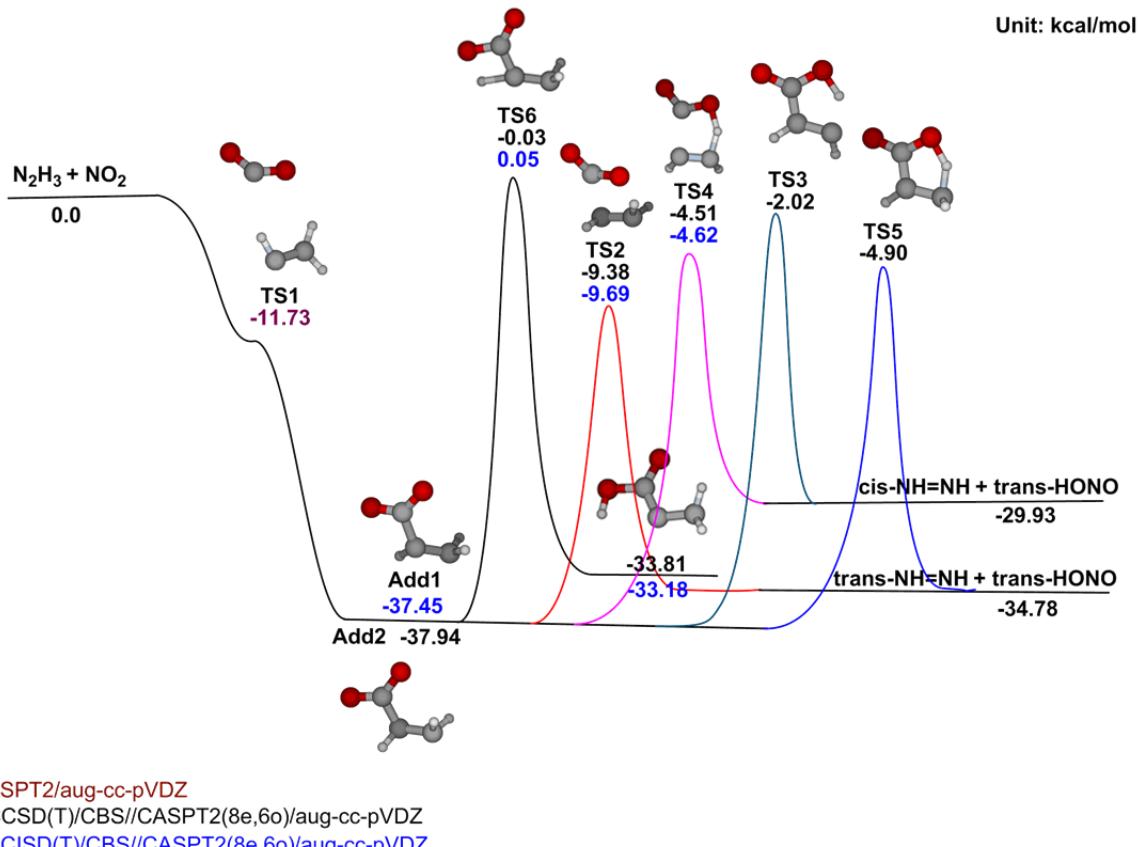
CASPT2/aug-cc-pVDZ  
RCCSD(T)/CBS//CASPT2/aug-cc-pVDZ

**Figure 1:** Potential energy surface of  $\text{NO}_2 + \text{N}_2\text{H}_3$  (abstraction) calculated at the RCCSD(T)/cc-pV $\infty$ Z//CASPT2/aug-cc-pVDZ level. Energies are zero-point corrected and relative to that of entrance channel at 0 K.

The most exothermic abstraction channel is reaction (R1), which has a submerged barrier of -5.70 kcal/mol via TSA1, forming an H-bonded product complex (PHBC1) with an energy of -39.57 kcal/mol. It then dissociates to the products trans-NH=NH and cis-HONO with an overall reaction energy of -34.55 kcal/mol. The abstraction of imidogen-H (R2) was found to have the lowest energy barrier of -12.88 kcal/mol via TSA2, which is due to electron donation from the N atom to the forming O—H bond. The reaction forms an H-bonded product complex (PHBC2) with an energy of -22.76 kcal/mol, which then dissociates to the products  $\text{NNH}_2$  plus cis-HONO with an overall reaction energy of -10.94 kcal/mol. Reaction (R3) has an energy barrier of -3.17 kcal/mol via TSA3 and it forms an H-bonded product complex (PHBC3) with energy of -19.39 kcal/mol, which then dissociates to the products  $\text{NNH}_2$  plus trans-HONO with overall reaction energy of -10.84 kcal/mol. The abstraction reaction by the less nucleophilic nitrogen of  $\text{NO}_2$  was found to be almost thermal-neutral, with energy of reaction of -2.73 kcal/mol. Even though the nitrogen is less nucleophilic than the oxygen in  $\text{NO}_2$ , the H-abstraction by the nitrogen of  $\text{NO}_2$  still has a negative energy barrier of -5.37 kcal/mol via TSA4 due to electron donation from the N atom to the forming N—H bond. The formed H-bonded product complex (PHBC4) from this channel has an energy of -14.15 kcal/mol. Overall, the four H-bonded product complexes are 5 to 12 kcal/mol more stable than the corresponding dissociation products, and it is noted that, at low and intermediate pressures, cis-HONO, trans-HONO, trans-NH=NH, and  $\text{NNH}_2$  are the favorable products.

## (II). N-N Addition Reactions

It was found that both the nitrogen and the oxygen of the  $\text{NO}_2$  can be added to the  $\text{N}_2\text{H}_3$  radical. For the case of nitrogen addition to the radical site in  $\text{N}_2\text{H}_3$  (N-N addition), as shown in Figure 2, two adducts are formed, which are optical isomers with energy of -37.9 kcal/mol.



**Figure 2:** Potential Energy surface of  $\text{NO}_2 + \text{N}_2\text{H}_3$  (addition) calculated at the RCCSD(T)/cc-pV $\infty$ Z//CASPT2/aug-cc-pVDZ level. Energies are zero-point corrected and relative to that of entrance channel at 0 K.

In Figure 2, adduct Add1 is formed with the imidogen-H in the front of the pseudo N-N-N-O plane, and Add2 is formed with the imidogen-H in the back of the pseudo N-N-N-O plane. By intrinsic reaction coordinate (IRC) analysis, it was found that the two isomeric adducts are formed via one saddle point, TS1, which has a planar structure with an energy barrier of -11.73 kcal/mol. Furthermore, no pre-reactive H-bonded complex is formed before the saddle point due to the presence of the strong nucleophilic O atom in  $\text{NO}_2$ . It was also found that each of the optical isomer adducts,  $\text{NH}_2\text{NHNO}_2$  have distinct transition states corresponding to intramolecular H-abstraction from the  $\text{NH}_2$  group to form trans- and cis- $\text{NH}=\text{NH}$ , and trans-HONO products. The Add1 adduct undergoes intramolecular H-abstraction via TS2 with an energy barrier of -9.38 kcal/mol to form trans- $\text{NH}=\text{NH}$  + trans-HONO products, and it also undergoes an intramolecular H-abstraction via TS3 with an energy barrier of -2.02 kcal/mol to form cis- $\text{NH}=\text{NH}$  + trans-HONO products. Similarly, the Add2 adduct undergoes intramolecular H-abstraction via TS4 with an energy barrier of

-4.51 kcal/mol to form cis-NH=NH + trans-HONO products, and it also undergoes intramolecular H-abstraction via TS5 with an energy barrier of -4.90 kcal/mol to form trans-NH=NH + trans-HONO products. For the intramolecular abstraction of imidogen-H, both adducts share the same four-member-ring transition state TS6 which has an energy barrier nearly identical to that of the entrance channel. This reaction channel forms NH<sub>2</sub>NNO<sub>2</sub>H as the intermediate with energy of -33.81 kcal/mol, which is stabilized by two internal H-bonds. The predominant channel in Figure 2 is the dissociation of Add1 via TS2, with an energy barrier of -9.38 kcal/mol, which forms trans-HONO + trans-NH=NH as the products.

For the case of oxygen addition to the N<sub>2</sub>H<sub>3</sub> radical, two adducts NH(ONO)NH<sub>2</sub> and NHNH<sub>2</sub>(ONO) are formed, which undergo further decomposition reactions. The potential energy profiles for oxygen addition pathways are currently under investigation.

### (III). Experimental Reaction Kinetics

Preliminary experimentations are currently underway to measure the rate of HONO production under pseudo-first-order conditions of [N<sub>2</sub>H<sub>3</sub>] in [NO<sub>2</sub>].

## 5. Conclusions

The potential energy profile of the NO<sub>2</sub> + N<sub>2</sub>H<sub>3</sub> reaction was investigated by *ab initio* multi-reference second-order perturbation theory and quadratic configuration interactions and coupled-cluster theories. For direct abstraction reactions, it was found that the most exothermic channel involves the formation of the trans-NH=NH plus cis-HONO products with reaction exothermicity of 34.55 kcal/mol. The abstraction of the imidogen-H of N<sub>2</sub>H<sub>3</sub> has the lowest energy barrier of -12.88 kcal/mol, forming the NNH<sub>2</sub> plus trans-HONO products. For the addition of NO<sub>2</sub> to the N<sub>2</sub>H<sub>3</sub> radical, it was found that the reaction proceeds via a complex mechanism. Specifically, both the nitrogen and the oxygen atoms of the NO<sub>2</sub> can add to the N<sub>2</sub>H<sub>3</sub> radical. The N–N addition adducts were found to have an energy of -37.7 kcal/mol, which undergo further dissociation reactions by intramolecular H transfer. The predominant channel for the dissociation of the N–N addition adduct has an energy barrier of -9.5 kcal/mol, forming the trans-HONO plus trans-NH=NH products.

The major products of the reaction system are the trans- and cis- forms of HONO and NH=NH, and NNH<sub>2</sub>. The negative energy barriers and large exothermicities of the reaction channels implicate significant importance in the early stages of hypergolic ignition of hydrazine and its derivatives.

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